

54. Catalysis with Evaporated Metal Films in a Flow System. Part I. The Hydrogenation of Benzene and Cyclohexene over Nickel.

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An apparatus has been developed which keeps metal films free from contamination to an extent sufficient to maintain constant catalytic activity when reactions are followed for 3—4 hr. in a flow system.

Hydrogenation of benzene over nickel films was studied between 0° and 50°, with results in general agreement with those obtained in a static system.¹ Hydrogenation of cyclohexene is 200 times faster than that of benzene at -34°, and the divergence increases with temperature.

Absolute-rate theory confirms that for benzene the slow step is the formation of adsorbed C₆H₈ but it does not distinguish between the three possible mechanisms, (a) reaction of gaseous hydrogen with adsorbed benzene, (b) simultaneous addition of two chemisorbed hydrogen atoms, or (c) reaction between a hydrogen atom and chemisorbed C₆H₇.

It is often difficult to follow a catalytic reaction involving gaseous reactants over evaporated metal films in a static system when the pressure of one of the reactants has to be kept below a comparatively small condensation pressure. Apart from the experimental difficulties in following the disappearance of a low pressure of the reactant or the formation of a low pressure of product, the reaction may be complete in a short time owing to the high activity of this type of catalyst. Reduction of the amount of catalyst is unsatisfactory because of the likelihood of contamination of the smaller surface of a light film as it is prepared. Reduction of the temperature aggravates the problem of following the reaction at increasingly low pressures and may even increase the *percentage* rate of reaction. The latter complication will occur when the activation energy of the reaction is lower than the latent heat of vaporisation (or sublimation) of the least volatile reactant and when the order of reaction with respect to this reactant is zero or negative. Thus, it seemed desirable to develop a technique for the use of evaporated metal catalysts in a flow system, in order to control the rate of reaction by reducing the time of contact between the reactants and the catalyst surface.

Hydrogenation of benzene vapour over nickel was selected as a suitable reaction by which the apparatus might be tested, because reliable data have been obtained for this reaction in a static system by Beeck and Ritchie.¹ At the same time, it seemed important to compare the rates of hydrogenation of cyclohexene and benzene under similar conditions. Smith and Meriwether² found that cyclohexene was hydrogenated 8 times faster than benzene when the reactions were carried out in the liquid phase, using solutions in acetic acid, over a bulk platinum catalyst. However, the activation energy for the hydrogenation of cyclohexene was only 2.4 kcal./mole and thus it is possible that diffusion in the liquid phase may have limited the rate of reaction under their conditions. Other evidence, *e.g.*, Anderson's result³ that cyclohexene is hydrogenated in less than 1 min. on an evaporated nickel catalyst at 0°, suggested that the cycloalkene is hydrogenated much more rapidly than the aromatic molecule. It was considered that a comparison of the kinetic data for the hydrogenation of cyclohexene and benzene with rates calculated by the transition-state theory might assist in the determination of the mechanism of the two reactions.

EXPERIMENTAL

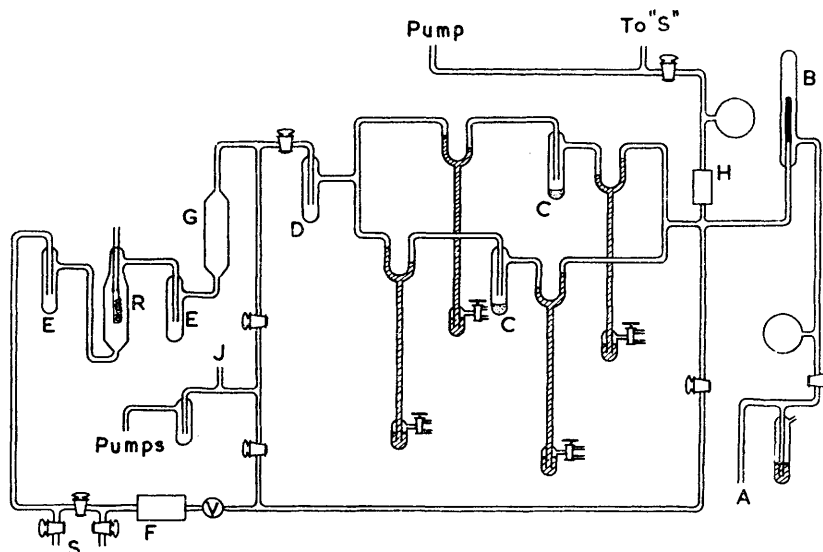
As a number of precautions were necessary to avoid contamination of the catalyst during each experiment, a detailed diagram of the apparatus is shown in Fig. 1. Hydrogen from a

¹ Beeck and Ritchie, *Discuss. Faraday Soc.*, 1950, **8**, 159.

² Smith and Meriwether, *J. Amer. Chem. Soc.*, 1949, **71**, 413.

³ Anderson, *Austral. J. Chem.*, 1957, **10**, 409.

cylinder, attached at A, was purified by diffusion through the palladium thimble B. The pressure of hydrogen was controlled by the device H which allowed excess of hydrogen to escape to the rotary pump through a sintered disc, normally covered by mercury but uncovered when the pressure rose to a predetermined value. Hydrocarbons were stored in either of the traps C and protected from contamination by the mercury cut-offs. During each run the appropriate trap C was maintained at a slightly higher temperature than trap D which controlled the partial pressure of hydrocarbon in the stream of hydrogen. The vessel G was packed with gold foil to remove mercury from the gases entering the reaction vessel R. The gold foil was purged periodically by heating it to 250° and passing a stream of hydrogen over it in the reverse direction. The reaction vessel was protected from stopcock grease by cooling the traps E during the preparation of the catalyst, and these traps were also cooled to the same temperature as trap D during each run. U-shaped sample tubes with stopcocks on each limb were attached at S to collect samples of the condensable gases for analysis by gas-liquid chromatography. Provision, not shown in Fig. 1, was made for the evacuation of each sample

FIG. 1. *Plan of the apparatus.*

tube so that there was no danger of air diffusing back into the reaction vessel when tubes were changed during a run. The flow-rate of hydrogen was controlled by the needles-valve V and measured by the calibrated flowmeter F. Pressures in the apparatus were measured by a McLeod gauge at J.

B.D.H. "spectroscopically pure" benzene and "laboratory reagent" cyclohexene were dried over sodium wire and dissolved gases were removed by repeated freezing and evacuation. The purity of both substances was checked by gas-liquid chromatography. Each catalyst was prepared from a 9" length of 0.5 mm. "pure" nickel wire (Johnson Matthey) coiled into a spiral which was attached by mild-steel connectors to 1 mm. tungsten leads sealed through the glass of the reaction vessel.

The reaction vessel was baked at 450° for 2 hr. at 10^{-5} to 10^{-6} mm. Hg, and the nickel wire was degassed by passing a current of 4.7 A for the final 30 min. of this period. The films were prepared with the reaction vessel surrounded by an ice-bath and a current of 6.4 A through the nickel spiral. In the early experiments, the catalyst was used without further treatment but in all the subsequent work the film was annealed for 30 min. at 50° in a pressure of a few mm. of hydrogen. The area of films treated in this manner was 890 cm.²/10 mg., as measured by the adsorption of krypton.* X-Ray investigation of the films indicated that they consisted of randomly oriented nickel crystallites.

The material collected in the sample tubes was analysed by gas-liquid chromatography

* Unpublished work by E. Crawford.

through a 6 ft. column of "dinonyl phthalate" supported on "Celite 545" at 45°, with detection of the compounds by thermal conductivity. Hydrogen was used as carrier gas at a flow-rate of 70 ml./min. and the pressure difference across the column was 45 cm. Hg with the input at atmospheric pressure. Peak areas were used in preference to peak heights for the estimation of the various hydrocarbons, and calibrations were carried out for each substance. Considerable tailing of the peaks occurred when the material was injected into the column directly from the sample tubes. Consequently, the technique was improved by distilling the material into a smaller space which was then heated according to a standard procedure before the hydrogen stream was passed through it in order to sweep the vapours into the column. Silicone high-vacuum grease was used on all stopcocks in the sampling system and the gas-liquid chromatographic apparatus.

RESULTS

Hydrogenation of Benzene.—The standard reaction mixture contained a partial pressure of 1 mm. of benzene and 100 mm. of hydrogen. This large excess of hydrogen was used in order to avoid undesirable side reactions such as the polymerisation of the unsaturated compound on the nickel surface.³

FIG. 2. Plot of the percentage conversion of benzene into cyclohexane against the reciprocal of the space velocity. Inset shows the influence of the pressure of hydrogen on the conversion at 20°.

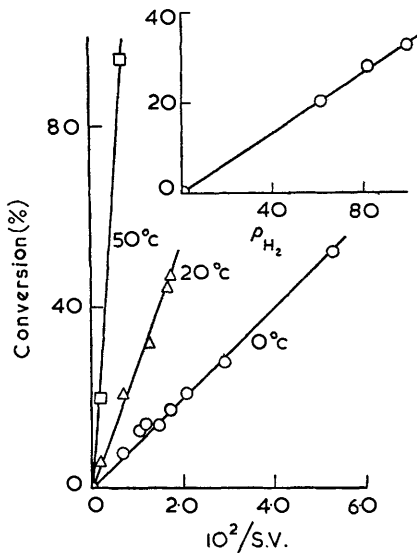
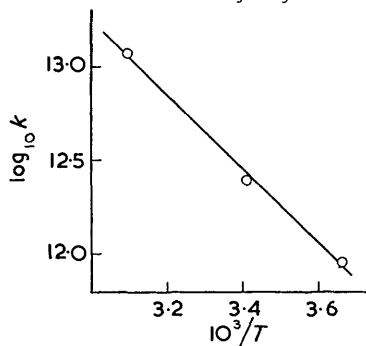


FIG. 3. Arrhenius plot for the hydrogenation of benzene (k is rate in molecules $\text{sec}^{-1} \text{cm}^{-2}$ of surface).



Early work with unannealed films revealed the presence of both cyclohexene and cyclohexane as products of hydrogenation of benzene at temperatures between 0° and 50°. Each sample was collected for about 20 min. The proportion of cyclohexene was substantially lower in the second and subsequent samples in each experiment, and as the results were not reproducible no kinetic data were obtained for the conversion of benzene into cyclohexene. This anomalous behaviour was almost eliminated by annealing the films in hydrogen at 50°; there were however still traces of cyclohexene in the first sample and evidence for a slightly greater production of cyclohexane than in the second and subsequent samples, these showing a steady catalytic conversion with no product other than cyclohexane for the duration of each experiment (normally 3–4 hr.). All further work was carried out with annealed films.

Typical results for the reaction at 0°, 20°, and 50° are shown in Fig. 2 as conversion against the reciprocal of the space velocity. This parameter was defined as the total volume (litres measured at S.T.P.) of gas flowing per hour per unit volume (ml.) of catalyst, and was evaluated by assuming that the density of the films was the normal density of nickel. The reciprocal

of the space velocity is a measure of the contact time between the reactants and the catalyst. Any influence of the reaction on the space velocity can be neglected as the reaction mixture contained only 1% of hydrocarbon. The linear plots are consistent with (a) a catalytic activity proportional to the volume, and hence the weight, of the nickel films and (b) a zero-order dependence of the rate of reaction on the partial pressure of benzene.

A series of experiments at 20° under identical conditions, except for the use of three different partial pressures of hydrogen, are shown in the inset of Fig. 2 and they indicate that the conversion is of first order with respect to hydrogen pressure.

The rate of reaction (k) in molecules $\text{sec}^{-1} \text{cm}^{-2}$ of nickel surface was evaluated from the equation $k = XQN/(22,400 \times 89w)$ where Q is the flow-rate of hydrocarbon in ml. (S.T.P.) sec^{-1} , N is Avogadro's number, X is the fraction of the benzene converted at a partial pressure of hydrogen of 100 mm., and w is the weight of the catalyst in mg. Rates obtained in this manner are shown in Fig. 3, and the Arrhenius plot corresponds to $E = 9.0 \pm 0.5$ kcal. mole^{-1} and $A = 1.5 \times 10^{19}$ molecules $\text{sec}^{-1} \text{cm}^{-2}$ of surface in the equation $k = A \exp(-E/RT)$.

Hydrogenation of Cyclohexene.—The standard reaction mixture contained a partial pressure of 1.26 mm. of cyclohexene and 40 mm. of hydrogen. Results obtained at -22.9° and -34.6° are shown in Fig. 4 and they are similar to those for benzene, given in Fig. 2, except

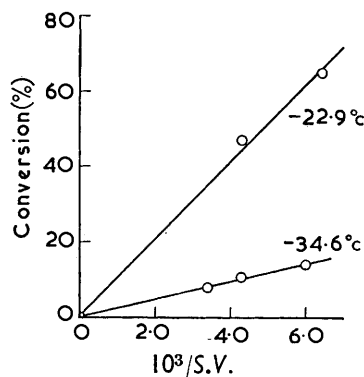


FIG. 4. Plot of the percentage conversion of cyclohexene into cyclohexane against the reciprocal of the space velocity.

that the reaction was much more rapid. It was not possible to obtain reliable data for the order of the reaction with respect to the pressure of the hydrogen because the palladium thimble would not deliver sufficient hydrogen to maintain the high flow-rate needed to control the rate of the reaction under higher partial pressures of hydrogen than about 40 mm. The reaction was also so fast that it could not be studied over a sufficiently wide range of temperature to derive an accurate activation energy. The average value of the rates at the two temperatures were 3.1 and 0.7×10^{13} molecules $\text{sec}^{-1} \text{cm}^{-2}$ of surface under the standard pressure of hydrogen of 40 mm., and these correspond to an activation energy of 15 ± 2 kcal. mole^{-1} . The straight lines in Fig. 4 indicate that the reaction was of zero order with respect to cyclohexene pressure, and no products other than cyclohexane were observed.

DISCUSSION

Our results for the hydrogenation of benzene are in general agreement with those obtained by Beek and Ritchie.¹ They found the activation energy to be 8.7 kcal. mole^{-1} which is close to our value of 9.0 kcal. mole^{-1} . They report a zero-order dependence on benzene pressure but a 0.44th order with respect to hydrogen pressure, whereas our rate was of first order for the hydrogen-dependence and this seems in better agreement with the results for other hydrogenations.⁴ By using the results given by Beek and Ritchie for a nickel film at 21.5°, it is possible to calculate the rate of the reaction as 2.5×10^{12} molecules $\text{sec}^{-1} \text{cm}^{-2}$ of surface (based on a size of their reaction vessel of 400 ml., an area of 900 $\text{cm}^2/10$ mg. nickel; their pressure-dependence is used to correct from an initial pressure

⁴ Smith in "Catalysis," Vol. V (ed. Emmett), Reinhold, New York, 1957, p. 175.

of hydrogen of 342 mm. to our standard pressure of 100 mm.). Our rate at this temperature is 2.9×10^{12} in the same units. The agreement is satisfactory considering that our films were sintered at 50° whereas theirs were sintered at 23° and also that they were working with a relatively low ratio of hydrogen to hydrocarbon with the possibility of some poisoning of the film. We conclude from the agreement between the two investigations that we have been successful in avoiding any substantial contamination of the surface during our experiments with the flow system.

It is interesting to compare the rate of hydrogenation of cyclohexene with the rate of exchange of cyclohexane and deuterium on nickel films examined by Anderson and Kemball.⁵ They found an activation energy of 10.8 kcal. mole⁻¹ and a rate at -34° of 1.1×10^{12} molecules sec.⁻¹ cm.⁻² of surface, using 1 mm. of hydrocarbon and 19 mm. of deuterium, whereas our rate of hydrogenation with 40 mm. of hydrogen was 7×10^{12} molecules sec.⁻¹ cm.⁻² of surface. The rate-determining step in the exchange is the conversion of adsorbed cyclohexyl radicals into gaseous cyclohexane molecules (this will be the same as the rate of dissociative adsorption of cyclohexane under the conditions prevailing in an exchange reaction). It is possible that the same rate-determining step is involved in the hydrogenation of cyclohexene and that a somewhat greater rate of reaction is obtained because the surface is more extensively covered with adsorbed cyclohexyl radicals in the hydrogenation than in the exchange reaction. It seems clear that the relative strengths of adsorption are cyclohexene > hydrogen > cyclohexane, and this means that the kinetics of the two reactions are quite different. The hydrogenation is of zero order with respect to olefin and probably of first order in hydrogen, whereas the exchange reaction, at any rate on palladium, is of first order with respect to cyclohexane and inversely dependent on the pressure of deuterium.

The rate of hydrogenation of cyclohexene at -34.6° , *i.e.*, 7×10^{12} molecules sec.⁻¹ cm.⁻² of surface, is some 200 times faster than the corresponding rate of 3.2×10^{10} for the hydrogenation of benzene under a pressure of 40 mm. of hydrogen. Even greater disparity between the two rates occurs at higher temperature because the activation energy for the hydrogenation of cyclohexene exceeds that for the hydrogenation of benzene, *e.g.*, the ratio at 25° is about 3000 ± 1500 .

Thermodynamic data⁶ indicate that the addition of a hydrogen molecule to benzene to form cyclohexa-1,3-diene is endothermic to the extent of 5.6 kcal. mole⁻¹. The remaining stages in the formation of cyclohexane are strongly exothermic and, consequently, we shall assume that the slow step in the hydrogenation of benzene is the conversion of adsorbed C_6H_6 into adsorbed C_6H_8 . The increase of heat content for this step will depend on the relative strengths of adsorption of the two species under the conditions used for the catalytic reaction as well as on the change of heat content given above. Three possible mechanisms will be considered.

Mechanism (1). The reaction takes place between a gaseous molecule of hydrogen and chemisorbed benzene which is assumed to cover the surface. The appropriate expression according to absolute-rate theory is closely analogous to that given by Glasstone, Laidler, and Eyring⁷ for the immobile adsorption of a gas on a surface. The rate is given by

$$v_1 = C_{H_2} C_B \frac{kT}{h} \frac{f^*}{F_{H_2} f_B} \exp(-\varepsilon_1/kT) \dots \dots \dots (1)$$

where v_1 is the rate of reaction in molecules sec.⁻¹ cm.⁻² of surface, C_{H_2} the concentration of hydrogen in the gas phase in molecules cm.⁻³, and C_B the concentration of adsorbed benzene in molecules cm.⁻² F_{H_2} , f^* , and f_B are the partition functions of hydrogen (at unit

⁵ Anderson and Kemball, *Proc. Roy. Soc.*, 1954, A, 226, 472.

⁶ Kistiakowsky, Ruhoff, Smith and Vaughan, *J. Amer. Chem. Soc.*, 1936, 58, 137, 146.

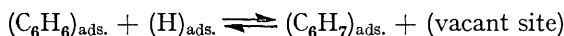
⁷ Glasstone, Laidler, and Eyring. "The Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 349

concentration), the activated complex, and adsorbed benzene respectively, and the other constants have the usual meaning.

Mechanism (2). The slow step is the addition of a chemisorbed hydrogen atom to a chemisorbed C_6H_7 species. The latter are assumed to be in equilibrium with adsorbed benzene molecules which cover almost all the surface and with hydrogen atoms which are weakly adsorbed on a fraction θ_H of the C_s sites available in the spaces between the benzene molecules. The value of θ_H is given by

$$\theta_H = \frac{C_H}{C_s} = C_{H_1} \frac{f_H}{f_s F_{H_1}} \exp(\epsilon_2/kT) \quad \dots \quad (2)$$

where f_s is the partition function of a site and the other terms require no definition. Considering the equilibrium



it follows that

$$C_{BH} = \frac{C_B C_H f_{BH} f_s}{C_s f_B f_H} \exp(\epsilon_3/kT) \quad \dots \quad (3)$$

The rate of reaction is given by

$$v_2 = C_{BH} \theta_H \frac{kT}{h} \frac{f^* f_s}{f_{BH} f_H} \exp(-\epsilon_4/kT) \quad \dots \quad (4)$$

and substitution from (2) and (3) gives

$$v_2 = C_B \theta_H^2 \frac{kT}{h} \frac{f^* f_s^2}{f_B f_H^2} \exp[-(\epsilon_4 - \epsilon_3)/kT] \quad \dots \quad (5)$$

and this expression reduces to (1) with

$$\epsilon_1 = \epsilon_4 - \epsilon_3 - 2\epsilon_2$$

after further substitution from (2).

Mechanism (3). The rate-determining step is the simultaneous addition of two adsorbed hydrogen atoms to chemisorbed benzene with other conditions as specified for mechanism (2). It is clear that the rate is given by expression (5).

It follows that it is impossible to distinguish by means of absolute-rate theory between these three mechanisms all of which correspond to a reaction which is of zero order with respect to benzene and first order with respect to hydrogen.

Evaluation of equation (1) using the experimental activation energy and assuming that a benzene molecule occupies 40 \AA^2 and that the ratio $f^*/f_B = 1$ gives a rate of 2.5×10^{13} molecules $\text{sec}^{-1} \text{ cm}^{-2}$ of surface at 25° and a pressure of 100 mm. of hydrogen. The experimental rate is a factor of 7 lower, *i.e.*, 3.5×10^{12} . This agreement is satisfactory considering the nature of the assumptions that have to be made. Further improvement in the agreement can be obtained if it is assumed that adsorbed benzene has greater freedom, *i.e.*, a higher partition function, than the activated complex. For instance, the adsorbed benzene molecule may have one degree of rotational freedom about the axis perpendicular to the plane of the ring which is lost when they form the activated complex. This would give $f^*/f_B = 1/4.4$ and bring the calculated and experimental rates into excellent agreement.

It is premature to attempt to calculate the rate of hydrogenation of cyclohexene until evidence is available about the order of reaction with respect to hydrogen pressure. However, it seems possible that some revision of the ideas about normal rates of hydrogenation may be necessary. The tendency at the present time is to regard the rates of

hydrogenation of cyclohexene and ethylene as normal and to consider the hydrogenation of benzene as unusually slow. Our calculations suggest that benzene reacts at the expected rate and hence that the catalytic hydrogenation of olefins may be abnormally rapid reactions.

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